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# **Triblock-Terpolymer-Directed Self-Assembly of Mesoporous** TiO<sub>2</sub>: High-Performance Photoanodes for Solid-State **Dye-Sensitized Solar Cells**

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A new self-assembly platform for the fast and straightforward synthesis of bicontinuous, mesoporous TiO<sub>2</sub> films is presented, based on the triblock terpolymer poly(isoprene-b-styrene-b-ethylene oxide). This new materials route allows the co-assembly of the metal oxide as a fully interconnected minority phase, which results in a highly porous photoanode with strong advantages over the state-of-the-art nanoparticle-based photoanodes employed in solidstate dye-sensitized solar cells. Devices fabricated through this triblock terpolymer route exhibit a high availability of sub-bandgap states distributed in a narrow and low enough energy band, which maximizes photoinduced charge generation from a state-of-the-art organic dye, C220. As a consequence, the co-assembled mesoporous metal oxide system outperformed the conventional nanoparticle-based electrodes fabricated and tested under the same conditions, exhibiting solar power-conversion efficiencies of over 5%.

## 1. Introduction

Dye-sensitized solar cells (DSCs) consist of three main device components: an electron-conducting network which is sensitized by a light-absorbing dye and surrounded by an

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electrolyte or hole-transport material.<sup>[1]</sup> Assembled in a laboratory from solutions of inexpensive chemicals, device efficiencies of more than 12% have been reported.<sup>[2]</sup> DSCs hence are a very promising candidate to contribute toward a balanced future energy solution.

High-performance DSCs rely upon an extremely high interfacial area because charge carriers are generated only in the chemisorbed monolayer of photoactive dye. Since the ground breaking work of O'Regan and Grätzel in 1991,<sup>[3]</sup> this is usually realized by the sintering of TiO<sub>2</sub> nanoparticles into a random network, which delivers over a 1000-fold increase in surface area in a 10 µm thick film, compared to a flat film. Significant progress has since been achieved, mostly by the

development of new sensitizers,<sup>[4]</sup> light management in the device,<sup>[5-7]</sup> and increasing the long term stability.<sup>[8]</sup> However, this long established champion photoanode faces serious limitations with the development of solid-state DSCs (ss-DSC) which employ an organic hole-transporter as the redox mediator.<sup>[9,10]</sup> Research efforts to replace the liquid electrolyte with a molecular or polymeric hole conductor are driven by the aim to increase efficiency by reducing the loss-in-potential<sup>[11]</sup> and to tackle stability issues caused by corrosion and leakage of the liquid electrolyte.<sup>[10]</sup> As charge carrier recombination in ss-DSCs can be up to two orders of magnitudes faster than in conventional liquid electrolyte devices,<sup>[12,13]</sup> the poor electron diffusion in these random networks<sup>[14-16]</sup> combined with limited infiltration of the solid-state hole transporters limit the titania electrode in ss-DSCs to around 2 µm. This is not thick enough to achieve panchromatic light absorption with the currently available sensitizers.

New electrode architectures have been proposed with the aim to control pore size and crystallinity on the 10 nm length scale in order to overcome these reported problems. Examples include geometries of standing nanowires,<sup>[17]</sup> fibrous 1D networks,<sup>[18]</sup> a bicontinuous gyroid network,<sup>[19]</sup> and the blockcopolymer directed assembly of sol-gel materials.<sup>[20,21]</sup> The latter is particularly promising because it allows control of pore size,<sup>[21]</sup> crystallinity,<sup>[22]</sup> and electronic properties<sup>[23]</sup> of the photoanode while being compatible with low-cost and large-scale production methods.

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The driving force for the self-assembly of block copolymers is the incompatibility of the covalently linked blocks of the macromolecule, which gives rise to a microphase separation on the 5-50 nm length scale into an assortment of morphologies with quasi-1D, quasi-2D, or quasi-3D continuity. This formation mechanism can be compatibilized with functional inorganic materials by taking advantage of selective interactions, such as hydrogen bonding, to drive sol nanoparticles into just one of the polymer blocks. After the removal of the organic host, typically in a high-temperature calcination step, the inorganic material then reflects the morphology derived from co-assembly. Wiesner and co-workers<sup>[24]</sup> and Stucky and co-workers<sup>[25]</sup> pioneered this method for structure directing silica, which was soon exploited for nanostructure control in TiO<sub>2</sub> and other metal oxides.<sup>[26-28]</sup> In principle, following this route should enable the design of ideal photoanodes with control over both morphology and feature size provided by the block copolymer. Indeed, blockcopolymer-derived TiO<sub>2</sub> has been shown to lead to enhanced electron mobilities when designed to facilitate high-temperature heat treatments.<sup>[29,22]</sup>

Despite the potential, DSCs incorporating self-assembled networks have still not reached the best efficiencies of nanoparticle based films. A major drawback is associated with the large volume contraction of the block-copolymer-derived films during processing—evaporation of residual solvent, condensation of the inorganic network, and, in the later stage, calcination of the polymer and crystallization. For films exceeding several hundred nm in thickness, this typically leads to crack formation and delamination.<sup>[30]</sup> Several concepts have been presented where block copolymer assembled photoanodes compete well with nanoparticle films for active layers below 1  $\mu$ m,<sup>[20,30]</sup> but it proves difficult to scale with thickness. We have recently established a route for the deposition of mesoporous block copolymer derived films beyond 2  $\mu$ m, which significantly increased their efficiencies to over 4%.<sup>[31]</sup>

An observed drawback of the experimental approaches used to date is the fact that the TiO<sub>2</sub> is generally assembled in the majority phase. Hence, lateral stresses during volume reduction are sufficient to lead to catastrophic crack formation. A further consideration is that the ratio between organic and inorganic material in the synthesis has a strong influence on the electronic properties of the resulting TiO<sub>2</sub>.<sup>[23]</sup> A mainly organic matrix leads to a strongly enhanced density of sub-bandgap electronic states, correlated to a significantly increased photocurrent in the devices. For both reasons, it would be favorable to lower the TiO<sub>2</sub> content in the hybrid composite. However, when reducing the TiO<sub>2</sub> content in a diblock copolymer assembled film, the metal oxide becomes a non-continuous minority phase surrounded by the polymer. Upon calcination of the oxide and thermal combustion of the polymer, film integrity is typically lost due to removal of the supporting matrix. We previously worked around this by performing calcination in the bulk, and subsequently incorporating the as-prepared material into a paste for film processing.<sup>[21,23,32]</sup> However, the favorable ordered structure of the mesoporous assembly is lost through this process. Clearly, a more direct route with a 3D continuous network morphology as-made would be preferable.

Here, we present a new self-assembly platform for the fast and straightforward synthesis of mesoporous TiO<sub>2</sub> films, based MATERIALS www.advenergymat.de

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on the triblock terpolymer poly(isoprene-*b*-styrene-*b*-ethylene oxide). This polymer system directs the co-assembly of the oxide into a gyroid-like morphology, where the minority phase is a 3D interconnecting strut network composed of  $TiO_2$ . A further less-intuitive benefit here is that the large organic fraction induces a high density of sub-bandgap states distributed in a narrow and low enough energy band, which maximizes charge generation in this dye-sensitized system. The material proves extremely effective when combined with the state-of-the-art organic dye C220 in solid-state cells, and we report power conversion efficiencies of over 5%.

#### 2. Results and Discussion

We have recently reported on the assembly of several network morphologies, including a 3D continuous alternating (single) gyroid niobia network, which arises from the co-assembly of a triblock terpolymer poly(isoprene-*b*-styrene-*b*-ethylene oxide) (PI-b-PS-b-PEO). In this configuration, the inorganic resides in the minority phase. Due to the fact that network phases are 3D continuous and self-supporting, the morphology is able to withstand removal of the polymer.<sup>[33]</sup> A similar system is used in this work. Figure 1a illustrates the chemical configuration: The triblock terpolymer in this work consists of a PI, PS, and PEO block with volume fractions of 31%, 53%, and 16% respectively. The introduced TiO<sub>2</sub> sol (blue particles) are expected to preferentially reside in the hydrophilic PEO block due to attractive intermolecular forces.<sup>[34]</sup> The incompatibility of its covalently linked building blocks leads the macromolecule and its guest to co-assemble toward its energy minimal morphology.<sup>[24,36]</sup> For the utilized volume fractions, we expect an ordered cubic network such as a single "alternating" gyroid morphology of PEO and inorganics, surrounded by a PS matrix and a complementary gyroid network of PI, as illustrated in Figure 1b.<sup>[33]</sup> For experimental realization, a PI-b-PS-b-PEO polymer (ISO) of  $M_{\rm n} = 53.4 \text{ kg mol}^{-1}$  was dissolved in anisole. Separately, a sol stock solution was prepared by adding titanium isopropoxide to HCl. The stock solution was then diluted and added to the polymer solution to match the aimed phase space. After deposition by doctor blade coating onto prepared fluorine-doped tin oxide (FTO) substrates, the films were annealed at 30 °C in an enclosed atmosphere for 24-48 h, then aged at elevated temperatures for another 3 days before being calcined in air at 500 °C to remove the organic structure directing agent and crystallize the inorganic network (see Experimental Section for details). The as-cast films had a homogeneously networked morphology throughout the thickness as shown in Figure 1c. The hybrid films were based on an oxide:polymer mass ratio of 0.33:1.0, assuming complete condensation to TiO2. This is equivalent to a volume uptake of 27.5% for the phase of PEO and  $TiO_2$ , that is, the TiO<sub>2</sub> being in the minority phase. The film thickness and overall amount of  $TiO_2$  deposited for each film was controlled with the solution concentration as well as the doctor blading height and velocity. The structural features were preserved throughout the crystallization process resulting in the generation of 20-30 nm mesopores as shown in Figure 1d. In contrast to earlier work using this triblock terpolymer to direct the structure assembly on more equilibrated morphologies in (a)



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Figure 1. Material system and morphology. a) The structure-directing macromolecule in this work is a triblock terpolymer PI-b-PS-b-PEO with volume fractions of 31%, 53%, and 16% for the isoprene (PI, gray), styrene (PS, light gray), and ethylene oxide block (PEO, dark gray), respectively. The introduced sol (black particles) are expected to preferentially reside in the hydrophilic PEO block due to attractive intermolecular forces. Under equilibrium conditions, the incompatibility of its covalently linked building blocks leads the block copolymer and its guest to assemble into its minimal energy morphology, which is in the present configuration an ordered network phase such as the alternating gyroid, where one gyroid network contains the PEO incorporating the oxide sol, and the second gyroid network contains the PI, surrounded by a PS matrix. b) One such gyroid containing the PEO and the oxide phase. c) Scanning electron microscopy image of a film deposited by doctor blade coating, shown after plasma etching to remove the polymer, which gives rise to a continuous, highly porous TiO<sub>2</sub> network. d) Close-up scanning electron microscopy image of the mesostructure top surface after calcination at 500 °C exhibiting open and accessible pores.

the bulk,<sup>[33]</sup> we cannot identify a specific space group due to the limited long-range structural ordering for thin film deposition. This is somewhat expected because drying kinetics in thin films lead to a quenching of the microphase separation process by the simultaneous sol–gel reaction before reaching its equilibrium morphology. Nevertheless, the  $TiO_2$  photoanodes exhibit a continuous network of very high porosity which arises from the co-assembly of  $TiO_2$  in the minority phase.

The as-calcined photoanodes were subsequently subject to a TiCl<sub>4</sub> treatment and resintering at 500 °C as is conventionally done for DSCs before being immersed in a dye solution and assembled into a solid-state DSC. Cross-sections of the fully assembled devices are shown in the Supporting Information. Crystallite sizes are ≈12 nm for the triblock-terpolymer-derived structures and ≈19 nm for the standard nanoparticle films via Scherrer analysis of the [101] anatase peak (see Supporting Information). The standard method to estimate the surface area and porosity of mesoporous oxides is to perform nitrogen desorption measurements. However, this proves difficult for thin films and furthermore a measure of the effective accessible surface area for dye adsorption may be more relevant for the electrode material. To estimate the surface roughness of the triblock-terpolymer-derived films, we therefore compared the accessible surface area by a dye desorption technique.<sup>[37]</sup> First, the standard nanoparticle-based films, which have been well characterized by nitrogen desorption, were used as a standard control. From nitrogen desorption, the standard nanoparticle films have a roughness factor of 116-fold per um thickness of film. Following overnight sensitization with a ruthenium based dye, termed Z907, and subsequent dye desorption, UV-vis absorption measurements of the desorbed dye were taken. The dye was calculated to occupy around 1.6 nm<sup>2</sup> per dye molecule, consistent with reports in literature.<sup>[38,39]</sup> With the assumption that same dye loading will be achieved on both the anatase titania triblock-terpolymer-derived films and the standard anatase nanoparticle-based films, we calculate the surface roughness to be 161-fold per µm thickness of film for the triblockterpolymer-derived films measured via Z907 dye desorption in methanol (see Supporting Information).

To estimate the porosity of the films we have used spectroscopic ellipsometry to extract the optical constants for each film, and subsequently reconstruct an "effective medium" composed of differing volume fractions of air  $(n \approx 1)$  and anatase TiO<sub>2</sub> ( $n \approx 2.5$  for  $\lambda = 632$  nm) employing the Bruggeman effective medium approximation.<sup>[39]</sup> The refractive indices of the films were determined to be 1.39 (triblock-terpolymer-derived films before TiCl<sub>4</sub>), 1.52 (triblock-terpolymer-derived films after TiCl<sub>4</sub>), 1.62 (nanoparticles before TiCl<sub>4</sub>), and 1.73 (nanoparticles after TiCl<sub>4</sub>), respectively at  $\lambda = 632$  nm. It is already apparent simply from these values that the porosity reduces slightly after TiCl<sub>4</sub> treatment and that the porosity of the triblock terpolymer films is higher than the nanoparticle films. Specifically, we calculate the porosity of the triblock-terpolymer-derived films to be  $69 \pm 2$  vol% before TiCl<sub>4</sub> treatment and  $61 \pm 3$  vol% after this surface treatment. In comparison, standard nanoparticle films before TiCl<sub>4</sub> treatment are calculated to be  $55 \pm 2$  vol% porous and  $48 \pm 4$  vol% after the surface treatment. The increase in refractive index after the TiCl<sub>4</sub> surface treatment corresponds to a  $\approx 1$  nm thick coating of the pore structure for both triblockterpolymer-derived films (average pore diameter ≈21 nm) and nanoparticle films (average pore diameter ≈18 nm), respectively (see ref. [40] for details). These porosity and surface area estimations indicate that structurally, the triblock terpolymer exhibits a



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Table 1. Film characteristics. Values shown correspond to films treated with TiCl.

Film	Porosity [vol%]	Surface roughness [µm <sup>-1</sup> ]	Crystallite size [nm]	Average pore diameter [nm]
Nanoparticle	$48\pm4$	116	19	18
Triblock	$61\pm3$	161	12	21

higher accessible surface are for dye loading as well as enhanced porosity compared to the standard nanoparticle-based films. A summary of all film characteristics can be found in Table 1.

Device characterization, shown in Figure 2, reveals the high efficiency of the presented photoanode. For comparison,



Figure 2. Current-voltage characteristics. a) Current-voltage curves measured under AM1.5 simulated sun light of 100 mW cm<sup>-2</sup> for devices incorporating triblock terpolymer co-assembled networks (black squares), diblock copolymer co-assembled networks (light gray triangles), and standard nanoparticle-based devices (gray circles) employing D102 as the sensitizer. Inset shows solar cell performance parameters for all three devices. b) Current-voltage curves for solid-state DSCs employing C220 as the dye sensitizer.

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which we have previously presented in a separate publication.<sup>[31]</sup> Solar cells fabricated from the triblock terpolymer, where the cast hybrid mixture has a majority component of organic material (around 70% by volume), show a comparatively high shortcircuit current  $(J_{sc})$  of 6.7 mA cm<sup>-2</sup>, and an open circuit voltage  $(V_{\rm oc})$  of 0.78 V. In the case of a diblock copolymer directed assembly, the TiO<sub>2</sub> resides in the majority phase, with a much higher inorganic to organic volume ratio after film deposition. These photoanodes show an increased  $V_{oc}$  of 0.83 V, whereas  $J_{\rm sc}$  is reduced to 5.8 mA cm<sup>-2</sup>. Devices based on conventional nanoparticle photoanodes lie in between, with  $V_{oc} = 0.80$  V and  $J_{\rm sc} = 6.5 \text{ mA cm}^{-2}$ .

These findings are consistent with previous observations of the role of the inorganic to organic ratio in the block copolymer assembly process upon the device properties of the photoanode.<sup>[23]</sup> The hybrid network within which the TiO<sub>2</sub> resides in during the calcination plays a decisive role for the electronic properties of the mesoporous TiO<sub>2</sub> even after the calcination step and TiCl<sub>4</sub> treatment. We have associated this to the reducing characteristic of the organics during polymer oxidation and TiO<sub>2</sub> crystallization at high temperatures. We speculate that the organic materials act as an oxygen sink, favoring the formation of oxygen vacancies which generate sub-bandgap states,<sup>[41-44]</sup> broadening the tail of the conduction band states, and subsequently aiding electron transfer from the photoexcited dye. A mainly organic matrix in the film preparation leads to a significantly increased generation of photocurrent, accompanied by a slight drop in  $V_{oc}$  in the final devices. Though photoanodes made from triblock terpolymer (highly porous continuous network), diblock copolymer (micellar arrangement), and conventional TiO2 nanoparticles (random dense packing) are all very different, a similar strong dependence on its "organic to inorganic history" during materials assembly has been observed.

For devices incorporating one of the best performing dves for solid-state DSCs, a donor-pi-acceptor organic dye termed C220,<sup>[46]</sup> we obtain a striking power conversion efficiency of 5.03% for triblock-terpolymer-directed photoanodes, shown in Figure 2b. This represents a 16% improvement in performance over standard optimized nanoparticle devices of 1.8 µm in thickness as prepared in our laboratory, demonstrating the potential of this approach for future high-efficiency devices. On a like-to-like comparison this is the first time the self-assembled oxides have outperformed the conventional state-of-the art nanoparticle based photoanodes in DSCs of optimum thickness. We note that the maximum current from the J-V curve for the triblock devices does not occur at short circuit. This effect is has been previously observed for some sensitizers when used in solid-state DSCs;<sup>[46]</sup> however, investigating its exact nature is outside of the scope of this work.

In our previous work on paste processed  $TiO_2$ , we eliminated the effect of the film morphology and found no significant differences in charge transport and recombination.<sup>[23]</sup> In contrast, here we observe over two-fold increase in charge transport rate at short circuit for films with diblock-copolymer-directed structures compared to the ones assembled with the triblock terpolymer (background bias light around 100 mW cm<sup>-2</sup>; see MATERIALS \_\_\_\_\_\_

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**Figure 3.** Device characteristics. Transport (a) and recombination (b) rates at short-circuit conditions for devices incorporating triblock terpolymer co-assembled networks (black, squares), diblock copolymer co-assembled networks (light gray triangles), and standard nanoparticle-based devices (gray circles). c) Density of states plot per cm<sup>-3</sup> of titania, for devices incorporating triblock terpolymer co-assembled networks (black squares), diblock copolymer co-assembled networks (gray circles), and standard nanoparticle-based devices (light gray triangles). Lines correspond to single exponential fits of the data points. We note that the transient photocurrent and photovoltage measurements were carried out at short circuit under potentiostatic or galvanostatic modes, respectively, with the short-circuit current set and varied by changing the white light bias.

Experimental Section for details). This trend is maintained over a wide span of light intensities down to 2 mW cm<sup>-2</sup>, which corresponds to a photocurrent of about 0.2 mA cm<sup>-2</sup> in these devices. This significant difference, shown in **Figure 3**a, probably arises from the larger crystal size (>19 nm) and the denser TiO<sub>2</sub> network of the diblock-copolymer-directed structures.<sup>[22,47]</sup> Recombination dynamics are very similar in all three systems, as shown in Figure 3b, where almost all data points overlap at similar background bias light intensities.

Along with higher electron transport rates, we would expect increased photocurrents from systems with better charge collection efficiencies. In contrast, we see a 15% loss in photocurrent for the "highly diffusive" diblock-directed films compared to the triblock systems. However, the charge collection efficiency, as calculated from the balance of rates for charge collection and recombination under short-circuit conditions, is over 95% for all systems. To resolve this peculiarity, we have performed differential capacitance–voltage measurements to reveal the shape of the sub-bandgap density of states (DOS) in the TiO<sub>2</sub> photoanodes. Figure 3c clearly shows a large increase in the sub-bandgap DOS for the triblock devices compared to the diblock solar cells. This effect is consistent with our postulation that the organic components partially reduce the surface



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of the TiO<sub>2</sub> during thermal degradation and calcination, with the more numerous oxygen vacancies increasing the density of sub-bandgap states. Indeed, others have reported that oxygen vacancies induce adjacent Ti<sup>4+</sup> ions which generate states ≈1 eV below the conduction band.<sup>[43]</sup> This suggests that the differences in photovoltaic parameters found in the J-V curves of Figure 2 are dominated by the underlying shift in the distribution of sub-bandgap states, rather than charge collection efficiencies, which is consistent with our previous work.[23] Accordingly, the available sub-bandgap states must be located at low enough energy levels to enable efficient electron transfer. On the other hand, the energy loss has to be minimized to avoid a trade-off between current and voltage and which would marginalize performance improvements. In the case of the triblock-terpolymer-derived structures, the sub-bandgap states are confined in a relatively narrow energy band, allowing us to maximize the photocurrent while still maintaining minimal losses to open-circuit voltage. This results in higher power conversion efficiencies than standard nanoparticle-based devices measured under similar conditions.

Because the transport rates are around two orders of magnitude faster than recombination rates at short circuit for all systems studied, we associate the improved functioning of our triblock-terpolymer-assembled photoanodes to the fact that we can engineer the metal oxide/dye/hole-transporter inter-

face to maximize the availability of sub-bandgap states for electron-transfer, while still maintaining a low enough recombination rate and high enough open-circuit voltage.

## 3. Conclusion

We have presented a new self-assembly platform for the fast and straightforward synthesis of mesoporous TiO<sub>2</sub> films, based on the triblock terpolymer PI-b-PS-b-PEO. Our material route has strong advantages over the state-of-the-art photoanodes employed in solid-state DSCs. From a purely materials basis, the terpolymer route enables the direct assembly of a continuous network of anatase TiO2 resulting in films with extremely high porosity and internal surface area. This assembled material is superior to the standard nanoparticle-based films on both dye-loading capacity (for a given thickness) and accessible pore volume. Electronically, the triblock-terpolymerderived TiO<sub>2</sub> exhibits a larger density of sub-bandgap states, than the standard nanoparticle-based material. This high availability of sub-bandgap states improves photoinduced electron transfer from the dye sensitizers. As a consequence, for the first time the self-assembled mesoporous oxide system



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outperforms the conventional nanoparticle-based electrodes fabricated and tested under the same conditions, with power conversion efficiencies of 5% demonstrated. We believe that further optimization in line with this work will most likely arise from decoupling the crystal size of the film with its morphology. Indeed, if bigger crystal sizes could be achieved without compromising the large availability of sub-bandgap states, surface area or porosity of the films, faster transport, and slower recombination can be expected, thus improving the charge diffusion length and hence the efficiency under working conditions.

#### 4. Experimental Section

Substrate Preparation: FTO-coated glass sheets (15  $\Omega$  sq<sup>-1</sup>, Pilkington) were etched with zinc powder and HCl (2 M) to obtain the required electrode pattern. The sheets were then washed with soap (2% Hellmanex in water), deionized water, acetone, methanol, and finally treated under an oxygen plasma for 10 min to remove any traces of organic residues. The FTO sheets were subsequently coated with a compact layer of TiO<sub>2</sub> (100 nm) by aerosol spray pyrolysis deposition at 450 °C, using air as the carrier gas.

*Electrode Fabrication:* Conventional nanoparticle film, a commercial anatase nanoparticle paste used (Dyesol 18NR-T), was diluted with ethanol at a ratio of 3 mL ethanol per 1 g of paste to obtain final film thicknesses of 1.8  $\pm$  0.1  $\mu$ m when deposited by doctor blade coating. The resulting films were subsequently calcined at 500 °C (ramped over 1.5 h) for 30 min in air.

Triblock-Terpolymer-Derived Film: A polymer solution was prepared by dissolving ISO (50 mg,  $M_n = 14.63$ , 29.04, and 9.77 kg mol<sup>-1</sup> for I, S, and O, respectively, with a polydispersity of 1.05) in anhydrous anisole (0.61 mL)for at least 1 h. In a separate vial a dilute sol stock solution was prepared by quickly adding titanium isopropoxide (5 mL) to concentrated 37 wt% HCl(aq) (1.6 mL) under rapid stirring. Caution must be taken because this addition is violently exothermic and can cause splashing. The closed vial containing the dilute sol stock solution was stirred for 5 min followed by the addition of dry tetrahydrofuran (10 mL) and two additional minutes of stirring. Next, the dilute sol stock solution (0.22 mL) was added to the polymer solution followed by 30 min of shaking. The quantity of titania sol added was chosen to correspond to ≈27.5 vol% for the combined PEO and titania volume to target the network morphology window.<sup>[49,50]</sup> Films were prepared by the doctor blade technique with the final solution onto an FTO substrate with a preformed titania compact layer deposited via spray pyrolysis. The wet films were allowed to dry on hotplates set to 30 °C for 1-2 days. The dry films were aged at 100 °C for 3 days to further the condensation reaction and then were calcined at 500  $^\circ\text{C}$  with a  $1\ ^{\circ}\text{C}\ \text{min}^{-1}$  heating ramp followed by a 1 h hold and natural furnace cooling.

Diblock-Copolymer-Derived Film: TiO2 electrodes were fabricated as follows: PI-b-PEO (0.4 g, molecular weight  $M_n = 34.4$  kg mol<sup>-1</sup>, 28 wt% PEO) was dissolved in an azeotrope solvent mixture of toluene (72.84 wt%) and 1-butanol (27.16 wt%) (8 mL). A titanium-containing sol was prepared separately by the addition titanium(IV) isopropoxide (1.54 mL, Sigma Aldrich, 99.999% trace metals basis) to hydrochloric acid 37% (aq) (0.49 mL) under vigorous stirring. Five minutes after addition of the titania precursor, the sol was added to the polymer solution and subsequently stirred for a further 30 min. Hybrid were then deposited from solution via spin coating (1800 rpm, 20 s) or doctor blading onto the prepared FTO substrates. Subsequently the films were exposed to an annealing protocol on a calibrated hotplate (2000 W with programme regulator, Harry Gestigkeit GmbH), typically for 10 min at 50 °C, followed by a 45 min linear heating ramp to 300 °C, and a final dwell time of 5 min at this temperature. The procedure of film deposition and subsequent annealing was repeated several times (typically 3-7

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cycles) to match the required film thickness. Finally, the stack was calcined at 600 °C (3 h, heat ramp 5 °C min<sup>-1</sup>, Cole Parmer, EW-33855-35) to remove the organic material and to crystallize the TiO<sub>2</sub>.

*Materials Characterization*: Scanning electron microscopy was carried out on a LEO 1550 FESEM (Zeiss) with a field emission source of 5kV acceleration voltage. Ellipsometric data were taken on a Nanofilm ep3se imaging ellipsometer and the instrument software was used to analyze the data. Results by imaging ellipsometry were verified with a spectroscopic ellipsometer (Woollam alpha-SE). Wide-angle XRD was performed on calcined films deposited on the FTO-coated glass as per device assembly. The measurements were made using a PANalytical MPD Pro using monochromatic CuK<sub> $\alpha$ 1</sub> radiation, using an X'Celerator linear detector.

Solid-State DSC Fabrication: The mesoporous electrodes were cut down to size and soaked in a TiCl\_4 aqueous bath (20  $\times$  10^{-3}  $_{\rm M}$ ) for 1 hour at 70 °C in an incubator. After rinsing with deionized water and drying in air, the films were heat treated another time at 500 °C for 45 min in air, then cooled down to 70 °C and finally immersed in a dye solution for 1 h. The dyes used were D102, (0.2 mm) in a 1:1 volume ratio of tert-butanol and acetonitrile and C220 (0.15 mm) in a 1:1 volume ratio of tert-butanol and acetonitrile. Spiro-OMeTAD was dissolved in chlorobenzene at varying concentrations ranging from 6 to 10 vol%. After fully dissolving the hole transporter, 4-tert-butyl pyridine (tBP) was added with a volume to mass ratio of 1:26  $\mu$ L mg<sup>-1</sup> *t*BP:spiro-OMeTAD. Lithium bis(trifluoromethylsulfonyl)imide salt (Li-TFSI) was predissolved in acetonitrile at 170 mg mL<sup>-1</sup>, then added to the hole transporter solution at 1:12  $\mu$ L mg<sup>-1</sup> of Li-TFSI solution:Spiro-OMeTAD. When changing the hole transporter concentration, these two ratios were kept constant. The dyed films were rinsed briefly in acetonitrile and dried in air for 1 min. Then a small quantity of the hole transporter solution (18-25 µL) was dispensed onto each substrate and left to wet the films for 15 s before spin coating at 700 rpm for 45 s in air. The films were left for a minimum period of 24 h in air before placing them in a thermal evaporator where 150 nm thick silver electrodes were deposited through a shadow mask under high vacuum ( $10^{-6}$  mbar).

Solar Cell Characterization: Simulated AM 1.5 sunlight was generated with an ABET technologies sun2000 Class AAB solar simulator calibrated to give 100 mW cm<sup>-2</sup> using an NREL calibrated KG5 filtered silicon reference cell. The spectral mismatch factor was calculated to be less than 1%. The *J*–V curves were recorded with a Keithley 2400. The solar cells were masked with a metal aperture defining the active area of the solar cells and the device holder and measuring apparatus is set up such that no light can enter the sides of the glass substrates. The photovoltage and photocurrent decay measurement<sup>[51,52]</sup> were performed as described elsewhere.<sup>[23,52]</sup>

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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